

# Development of Ion Milling Methods for SEM Imaging of the Utica Shale

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## **Abstract**

With the development of technologies such as horizontal drilling, shale formations that are amenable to resource extraction with unconventional methods are becoming ideal source rocks. The Utica Formation is currently of great interest and is already producing natural gas in many areas. While extensive research has been done on the properties of other gas shale formations such as the Eagle Ford, very little is known about the Utica Formation. This study focuses on determination of the size and shape of micro-scale pores in clays and carbonates, the formation of pyrite, and the occurrence of organic matter in Utica shale samples, as determined with two-dimensional images acquired on a scanning electron microscope (SEM). Polish to the level of precision necessary to obtain high quality SEM images is challenging for a soft rock such as shale. This research involved methods development for development of such a high quality surface. Acquisition of SEM images of well-polished samples allows observation and interpretation of micrometer to nanometer-scale pores and the minerals and organic material associated with the pores. In addition, this project compares Utica micro textures to those found in other resource-producing shale formations to predict whether it would behave similarly in terms of its petrophysical properties.

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# 1. INTRODUCTION

## I. Utica Formation

As easily accessible fossil fuels decline, energy resource extraction is driven toward unconventional methods such as horizontal drilling. Gas shales are currently gaining interest because of the success of shale plays such as the Barnett, Marcellus, Haynesville, Woodford, and many others (Curtis et al., 2012). The Utica Formation is composed of organic-rich shale that formed in the Appalachian Basin during the Ordovician Period. The Utica Formation is already producing and is becoming a targeted formation by many companies (Hill et al., 2014). Historically speaking, until recently gas shales have been greatly ignored and thus the microstructures and the relationships among porosity, organic matter and mineralogy of such shales are mostly unexplored (Curtis et al., 2012).

During the building and forming of the Appalachian Mountains during the Ordovician, a large basin was formed. Fine-grained sediments and organic material that settled in deep, anoxic parts of the basin became the black and grey shales that we observe today, including as the Utica Formation (Goldman et al., 1999).

The Utica Formation is composed of black shale, which is fine-grained mudrock with variable composition. Major rock-forming minerals include clay minerals and other phyllosilicates, carbonates, quartz, and feldspars along with organic material. Shale is fissile mudstone, often fossiliferous, that is distinguished by mm to cm scale laminae approximately parallel to the plane of bedding. The dynamics of sedimentation have given rise to variable compositions over both the micro and macro scale. Black Shale is rich in organic matter and forms in anoxic low energy environments such as deep ocean basins (Blatt et al., 2006).

Drill core samples from multiple sites in Ohio were acquired from Chesapeake Energy Corporation. The depths of the samples are known. Two samples were studied; one from relatively shallow depth (approximately 3,000 feet) and one much deeper (approximately 10,000 feet). Samples are from Richland County and Washington County, approximately 130 miles from one another.

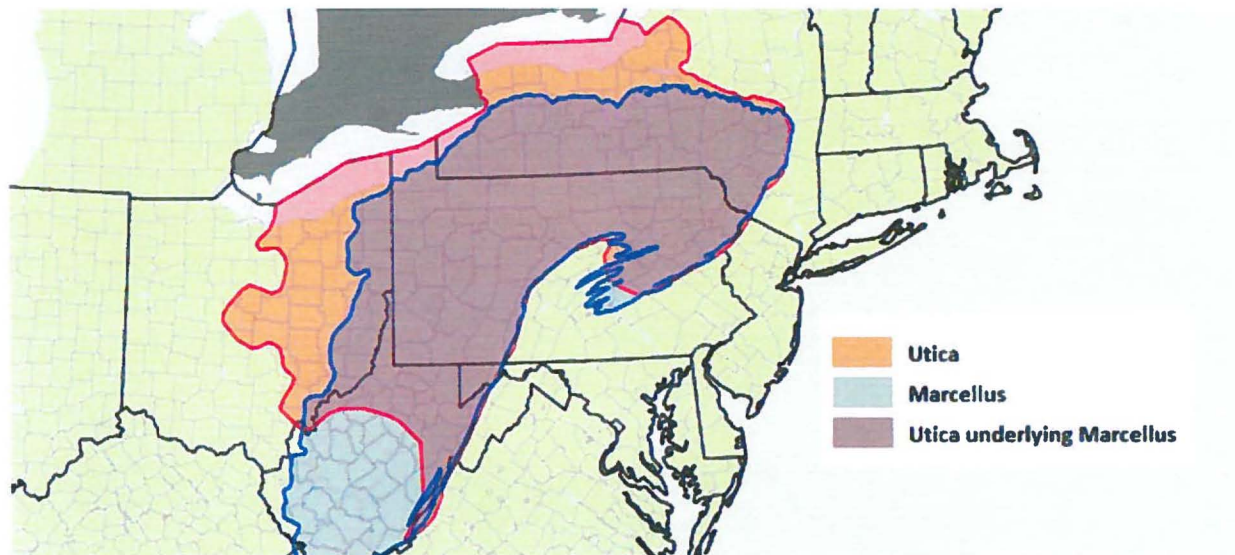


Figure 1: Distribution of the Utica Formation from [oilindependence.org](http://oilindependence.org).

## II. Objectives and Questions

The main objective of this study is to determine micron- and nanometer-scale features present in the Utica Formation, and compare them to well-characterized shale formations such as the Eagle Ford. One hypothesis states that the size, arrangement and composition of microstructures are directly related to petrophysical properties (Elgmati et al., 2011). Interpretation of microtextures in the Utica can help test this hypothesis, provided that petrophysical properties can ultimately be linked to these observations. In turn, information gained from the architecture of the Utica could influence approaches toward extracting its resources.

Questions for this comparative study include:

- 1) Are phyllosilicate pores in clay-rich regions triangular and linear in shape and are they variable in size, as seen in the Haynesville, Eagle Ford, and Fayetteville (Curtis et al., 2012)?
- 2) How are fossils related to pore structure and mineralogy?
- 3) Do clay minerals occur in pockets of interstitial pores along calcite grain boundaries, as observed in the Pearsall (Kanitpanyacharoen et al., 2012)?
- 4) How does pyrite form and contribute to micro-pore structures as seen in the Horn River, Toarcian, Pearsall, and Eagle Ford shales (Curtis et al., 2012; Loucks et al., 2012; Kanitpanyacharoen et al., 2012)?
- 5) Does organic matter appear as a spongy texture with nanoscale pores, as typically observed in the Barnett and the Pearsall shales (Loucks et al., 2012; Kanitpanyacharoen et al., 2012)?

These questions will be addressed using light and electron microscopy of sufficiently polished samples.



## **2. METHODS**

### **I. Sample Preparation for Microscopy**

The samples start as rough drill core. The first step was to drill and cut thick round sections which were then made into thin sections approximately 150 $\mu$ m thick, cut perpendicular to bedding and affixed to 1 inch round quartz slides. To obtain quantitative data from measurements of micron- to nanometer-scale rock textures, samples must be prepared such that they are nearly planar (with variation less than 15 micrometers across the surface of a thin section) with a sub-micron polish. When this level of precision is achieved, relatively large areas of a thin section can be observed to interpret small-scale features such as pores, fossils, organic material, and mineral grains using light and electron microscopy. Due to the mineralogical heterogeneity of black shale, it is a very challenging rock to prepare.

### **II. Cutting and Drilling**

The rock samples start as pieces of drill core of various sizes with way up typically indicated by the orientation of colored lines (red line on right means core is oriented in the up position as it was obtained from the well). The first step is to determine where to drill and to cut thick sections from the original core sample. This is decided by finding a spot that is easily accessible and preserves as much of the original sample as possible for future research. The samples are drilled using a drill press set to a slow speed. The drill bit used has a circular opening with a diamond cutter. This leaves behind a “puck” approximately 2.5 cm in diameter. Cool water must be running over the sample during the entire drilling process to maintain temperature and to flush away particulates. When turning the handle to bring down the drill bit, low pressure should be used and works best with a soft pulsing motion. By pulsing, the water is constantly flushing out the rock powder from the area being drilled and avoids putting excessive



stress on the drill press or the rock. Once the circular cutter has penetrated to a certain depth, the puck is cut free using a rock saw. Figure 2 shows a puck that has been drilled but not yet cut.

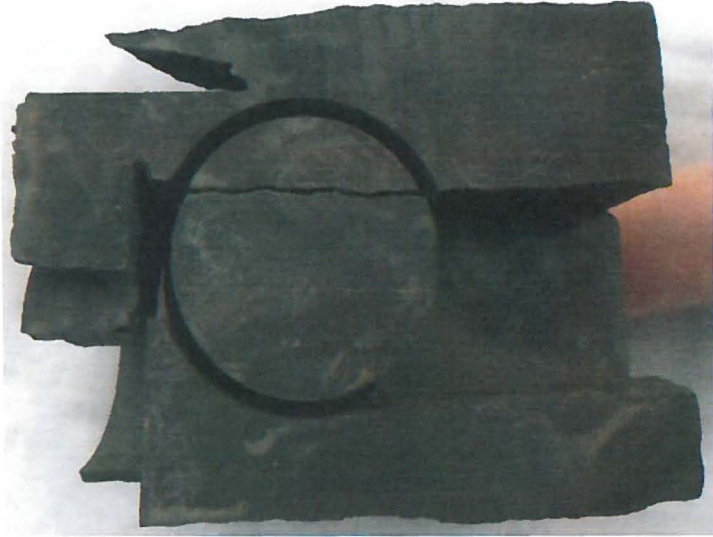


Figure 2-Core post drilling, pre cutting.

Like the drill press, the rock saw operates using a fluid, typically a mixture of water and a minor amount of oil. Once the rock saw is prepared with proper fluid, the sample is mounted in the saw with the orientation of the blade perpendicular to the drill's circular cut. The cutting is watched closely so the saw can be stopped the moment the thick sub core falls free from the sample. Figure 3 is a picture of the original sample with the sub core both drilled and cut out.



Figure 3-Core post drilling and post cutting

These samples were then cut into billets and sent to an outside vendor to make approximately 150 micrometer-thick rock sections, prepared on quartz for neutron scattering. After neutron scattering the samples are ready to be prepared for SEM work.

### **III. Flatness vs. Roughness**

There are two main variables in describing a high quality surface, flatness and roughness. Flatness is a regional property that is defined by a geometrical zone between two parallel planes in which the surface must lie. For example, if a regional area is all within 1000–1005 meters above sea level, that region is flat. If the region varies between 500 and 1500 meters above sea level, that is not a flat area. Roughness represents the quality of polish and is determined by peaks and valleys on the surface. Figure 4 is schematic representing these properties.

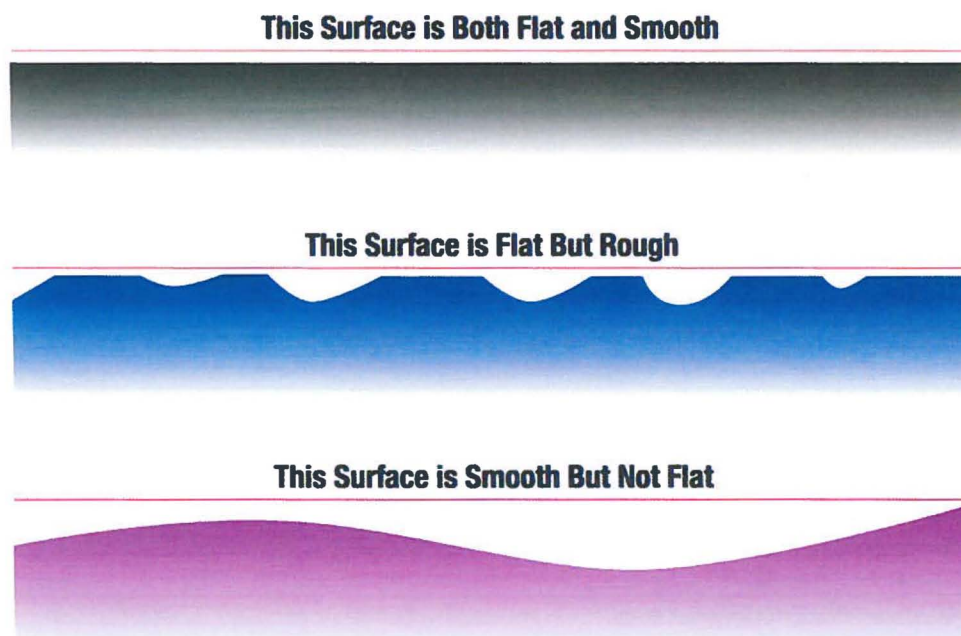


Figure 4-Schematic representation of flatness and roughness. Image from Thor Labs.

#### IV. Flattening Sample

To make a sample flat, high spots must be preferentially ground away without grinding low points, until all spots lie approximately in the same plane. First attempts employed an automated method with machinery, but the results were not adequate. After many different approaches with grinding tools, a mechanical process done by hand, called lapping, was adopted. Lapping is the process by which an abrasive flat surface is used to grind sample until the sample matches the flatness of the abrasive surface. To find high points the sample is wobbled and then rotated slightly until the largest wobble is found. The hinge of the largest wobble represents the axis of the highest point. Once the hinge of the largest wobble is found, the sample is gripped and rubbed parallel to the hinge against the abrasive flat surface. This is done until the wobble is gone along the hinge. Once wobble is gone, sample is rotated once again until the new largest wobble is discovered, and then the process is repeated until the sample has no wobble. This



process is repeated until the sample has no wobble, representing a flat sample that has been lapped to the flat abrasive surface. For the Utica shale samples, the abrasive flat surface was a copper plate with 20-micrometer diamond grit embedded into the plate. The time it takes to complete this process depends on the sample.

## **V. Polishing**

Shale is soft and heterogeneous, which makes it challenging to acquire an even polish. Because of the soft nature of shale, large force in isolated areas can rip into the rock. This means a very small and gradual force must be applied in order to remove roughness without damaging the sample. The sample being flat helps with polishing because it lowers the force applied to the sample.

$$F=P/A$$

F is the force applied to the sample, which is determined by P, pressure, and A, area. By increasing the area of the sample, the force is distributed over the sample, and thus is less destructive in isolated areas. To polish the sample, a Buehler Mini-Met 1000 was used. With Buehler Crystalbond LTepoxy, the sample is mounted onto a sample holder. The sample holder found to work best is designed for rectangular thin sections, but circular slides can still be attached using the epoxy. The sand paper is placed on a glass disk which goes inside a plastic bowl. This bowl is then filled with a lubricant and locked into place on the Buehler Mini-Met 1000. The lubricating fluid used is ethylene glycol. Figure 5 shows the set up.





Figure 5- Buehler Mini-Met 1000 with sample ready to run.

After the Buehler MiniMet 1000 is set up, the sample is pushed against abrasive diamond grit paper or plate and then grinding process is started. Because samples were lapped using a 20 micrometer diamond grit plate, the level of roughness on the sample starts out at 20 micrometers. The 6 micrometer diamond grit disk was found to be the most efficient step from the 20 micrometer plate. It has high enough grit to work away deeper scratches over time but small enough grit to prevent digging in new scratches. The sample was run on a 6-micrometer diamond grit for 1–2 hours, and progress checked every 30 minutes. The sample is evaluated with a hand lens as it is polished until no deep scratches are visible. When satisfactorily polished with 6 micron grit polish, a new bowl is acquired and a diamond grit paper of 3 micrometers mounted on a glass disk and used. The sample is typically run for 2 hours with the 3 micrometer diamond grit paper. Finally, the 1 micrometer diamond grit paper is used to finish the polish, being run for 2–3 hours. To determine quality of polish, a Leica DMS 1000 light optical microscope was used to observe how the sample reflected light. Images are recorded digitally using software available on the Leica as sample polishing progresses.

Pyrite plucking becomes a major issue in the final phases of grinding. Commonly pyrite grains will be plucked from the sample and become embedded in the diamond grit paper. With pyrite grains being a few micrometers in size and a Mohs hardness of 6–6.5, this embedded pyrite scratches the sample as it is ground, destroying the polish. Figure 6 is an image of a pyrite grain embedded in sand paper acquired on the light optical microscope. The pyrite grain is more than 10 micrometers in size and can ruin a surface with deep scratches. To deal with this issue, the lowest possible speed and pressure were used, and the sample is bathed completely in ethylene glycol. This prevented any pyrite plucking and allowed for adequate polishing.

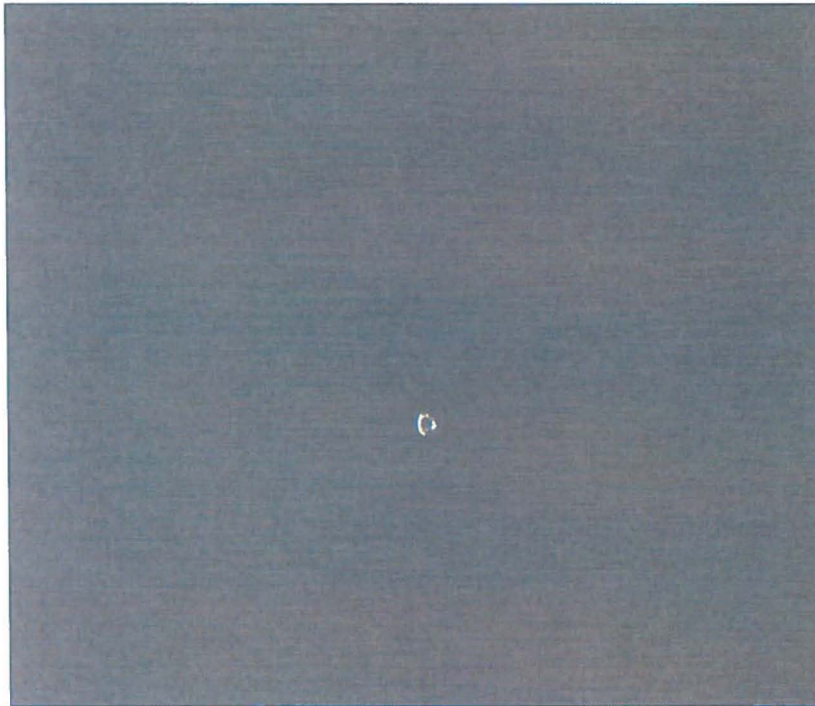


Figure 6- Pyrite grain embedded in 1 micrometer diamond grit paper.



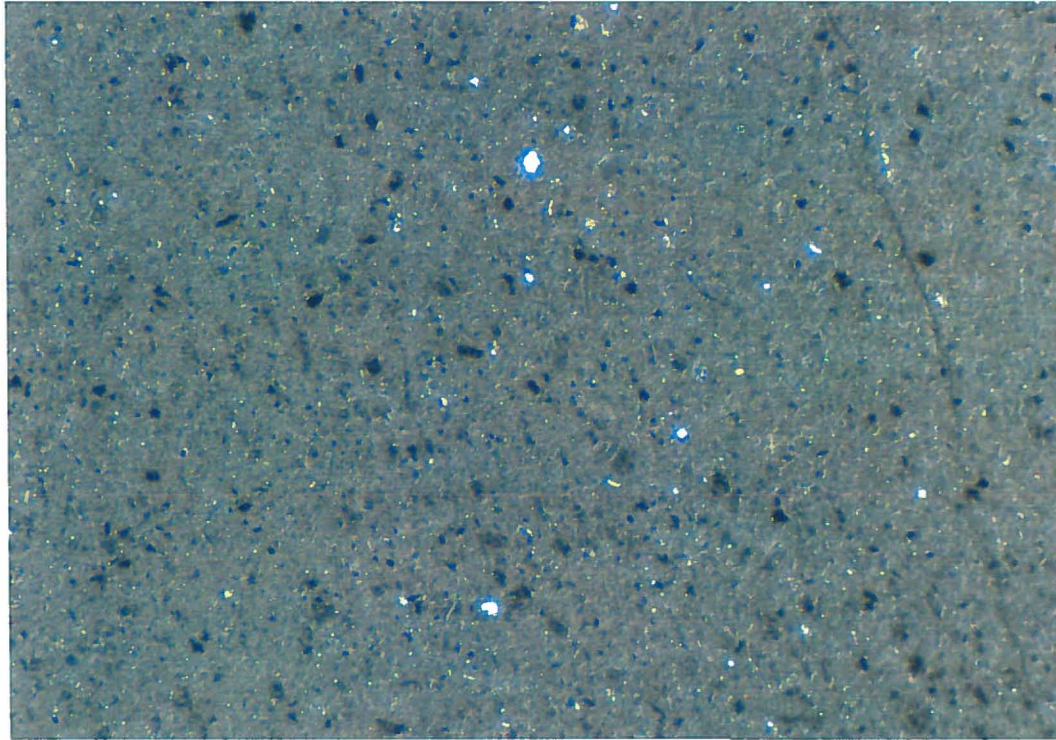


Figure 7-Sample with sufficient polish.

Figure 7 shows a satisfactory polish imaged with the Leica digital light optical microscope. There are no visible scratches, and the sample is reflecting light. This level of polish yields a large surface area for observation with the SEM. However, mechanical polish is limited by the size of the smallest grit used for polishing. Ion milling greatly increases the quality of images, which in turn aids the interpretation of micro-structures and features (Curtis et al., 2012; Loucks et al., 2012; Kanitpanyacharoen et al., 2012).

## VI. Ion Milling

Ion milling polishes the sample by firing ions at the surface as the sample rotates. The ions hit the surface at an angle which sputters material away. The variables that can be controlled in the ion mill are gun angle, voltage (and therefore current), and the length of time that the sample is run. Gun angle determines the angle at which the argon ions strike the surface. Lower angles can cause smearing and scalloping while higher angles rip into the surface and cause chiseling and streaking.

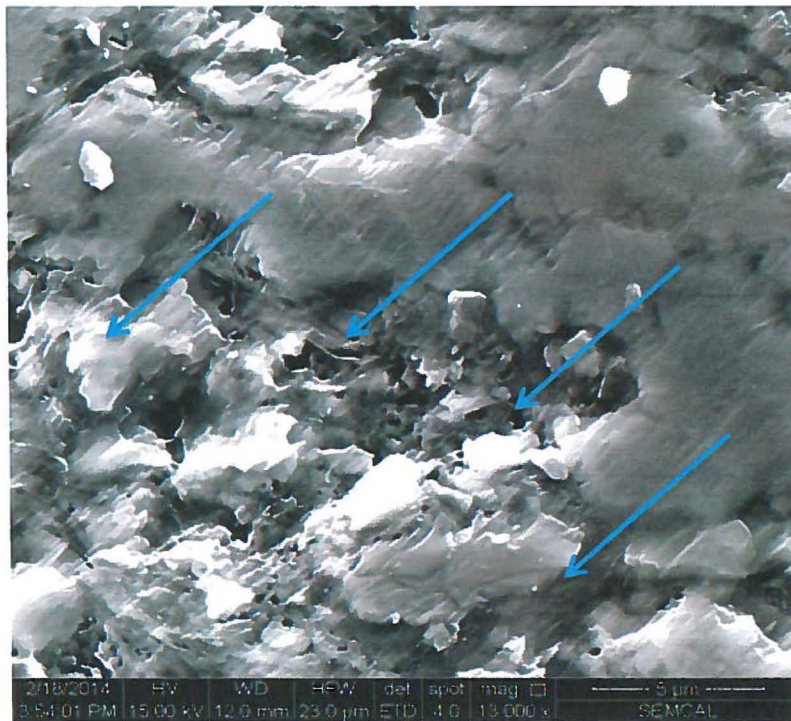


Figure 8-SEM image showing ripping of surface (Arrows show streaking direction).



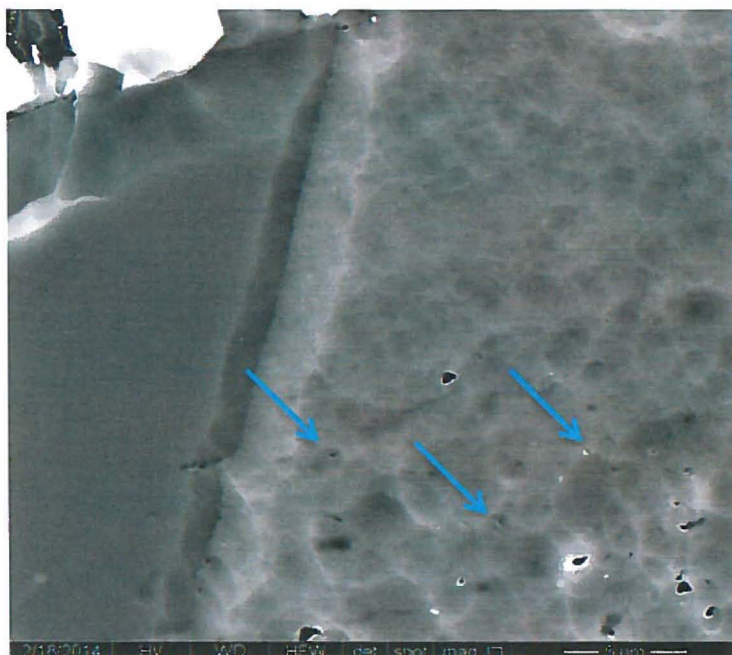


Figure 9- SEM image of smearing of surface (Arrows show smeared pores).

Ion milling artifacts may confound the interpretation of micro features or distinguishing pores from plucked grains (Figure 8). Figure 9 shows an example of scalloping and smearing. Smearing yields pores that have had material pushed over them, which can make interpretation about pore size and shape difficult. A low gun angle ( $<7$  degrees) with relatively low voltages ( $<2.5\text{keV}$ ) worked best. Sputtering is improved, but the lower voltage helps to decrease chiseling and streaking.

When ion milling attempts were first made, long run times were used (3–4 hours). This was found to be too destructive to the sample. The best results were obtained using a short run time, low angle, and low voltage. The values that yield the best results are: voltage =  $2.2\text{ keV}$ , gun angle =  $5$  degrees, and time =  $20$  minutes. The short run time is a surprising result.

In order to mount the sample in the ion mill a stage is used to set the eucentric height of the surface in the ion mill. When using heat sensitive epoxy (Buehler Crystalbond LT) a sample was lost into the machine because the sample heats up during argon ion bombardment. Copper

tape or super glue should be used instead, although super glue makes removal of glass slides challenging. During this study, ion-milling yielded a high quality of polish over an area that is approximately 1 cm in diameter.

## **VI. Scanning Electron Microscope**

The scanning electron microscope (SEM) uses a focused beam of electrons to scan a surface and generate signals from which images are obtained. The FEI Quanta FEG 250 SEM available in the Subsurface Energy Resources Characterization and Analysis Laboratory (SEMCAL), School of Earth Sciences, The Ohio State University, can also perform energy dispersive spectroscopy (EDS) to identify major and minor elements from a micrometer-scale spot on a sample. The interactions of the atoms in the sample with the focused beams of electrons produce signals that can be detected that can yield elemental composition and surface topography. The electron beam's position is combined with a detection signal to interpret the scattering of electron beam and allow the acquisition of a digital image. SEM can achieve high resolution to the 10s of nanometers scale. The majority of micro pores and features in mudrocks are generally smaller than a few micrometers in diameter and cannot be seen using light optical microscopes (Loucks et al., 2009). The SEM has two different detectors for the scattered electrons, backscattered electrons (BSE) and lower-energy secondary electrons (SE). SE images give an accurate representation of surface topography while BSE images show atomic number contrast, thereby indicating compositional differences. For example, pyrite and fossils in shale are very easy to see in the BSE because Fe in the pyrite and Ca in the carbonate are relatively high atomic mass elements, which gave a greater backscattered electron yield. Topographical peaks and valleys are much better seen in SE images. Before a sample is run, it is sputter coated with Au and Pd to minimize charging effects. The sample is then mounted onto a thin section

SEM sample holder using carbon tape. The sample can be viewed under high vacuum or low vacuum (in the case of no sputter coating). Due to the large surface area of the sample, many images can be taken over a wide region relative to the micrometer scale.



### 3. DISCUSSION

#### I. Polishing

Surface features fashioned into the surface during sample preparation may yield misleading information if the rock is not flat but instead possesses topography. For example, if a grain is plucked it appears as a large pore. On the other hand, surface area achieved by a combination of mechanical polishing and ion milling produces high quality SEM images. From these images observations of different micro-features can be observed such as micro-pore shape and size, pyrite formation and crystal habits, and organic material. Figure 10 displays an image acquired in the SEM, taken right at the boundary between a low point that was not polished (left) and a polished surface (right).

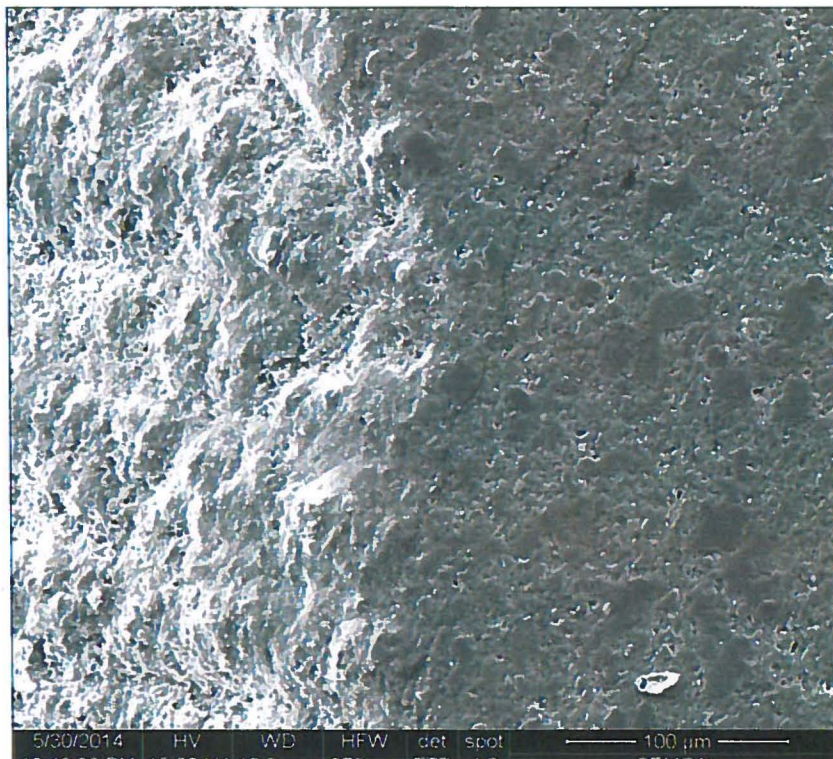


Figure 10-SEM image of boundary between unpolished and polished surface



## II. Clay Minerals and Carbonate Zone Porosity

Clay-rich zones have been associated with micro-pores that occur in a variety of shapes and sizes. Typically, the clay minerals are platy and closely packed together forming triangular and linear pores as described for the Haynesville, Eagle Ford, and Fayetteville (Curtis et al., 2012). Images acquired of the Utica formation display these same features. As shown in Figures 11 and 12, the pores form slit shapes that are triangular or linear. Nano scale porosity in gas shales has been found to average 0.05–0.5  $\mu\text{m}$  in diameter with a highly variable length (Elgmati et al., 2011). Figures 11 and 12 (Utica) show that the sizes and shapes of the pores are similar to other gas shale plays. It is clear that the porosity associated with clay have a similar morphology.

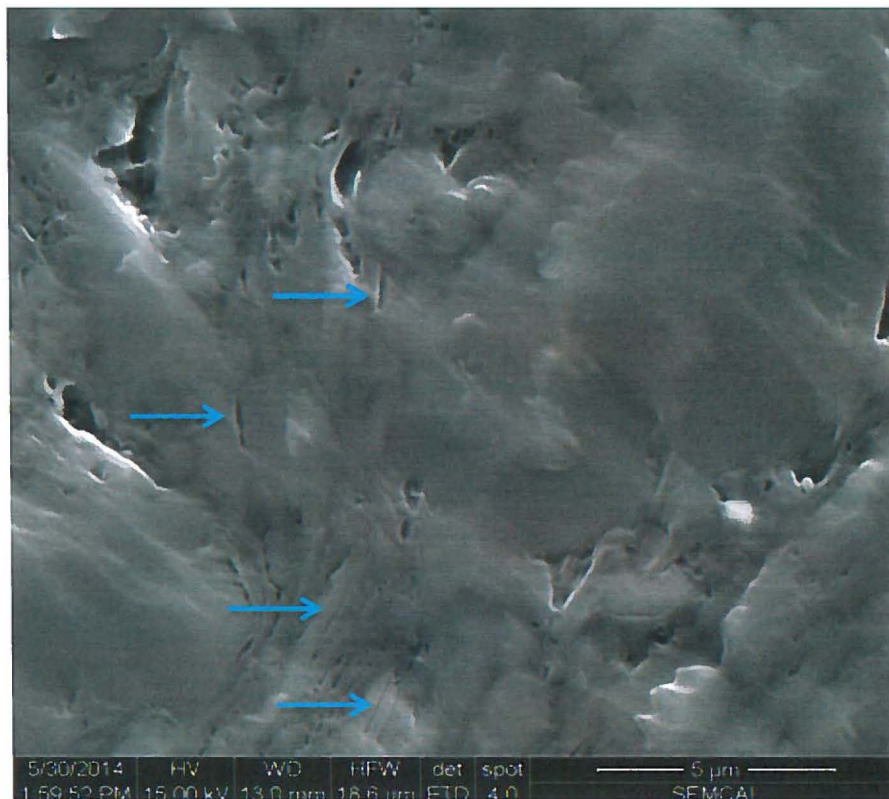
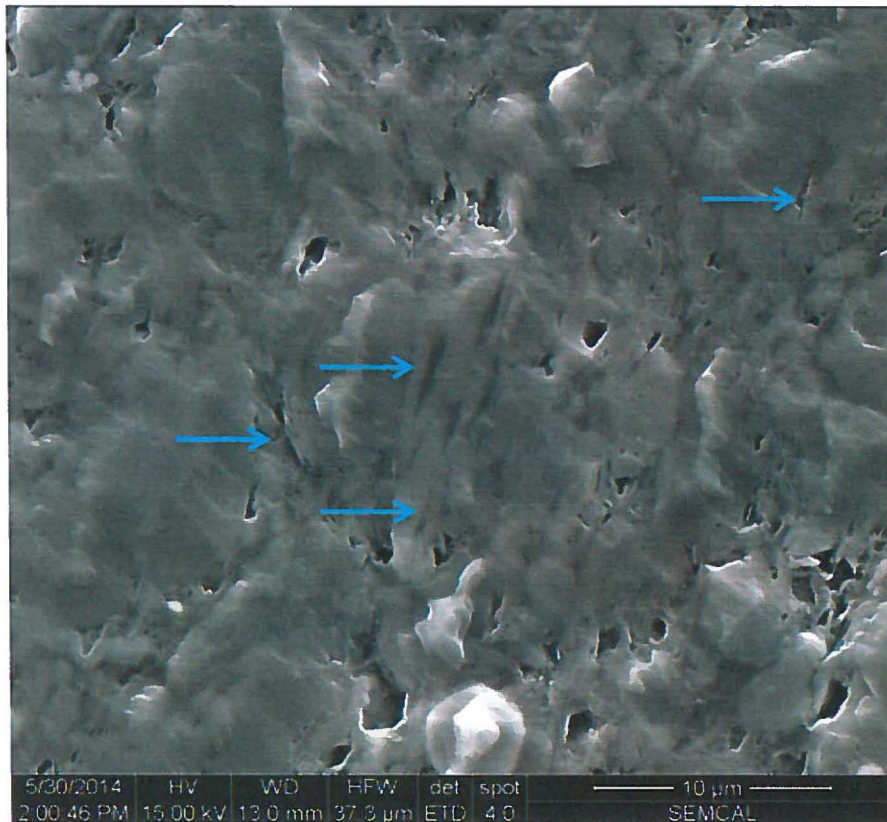


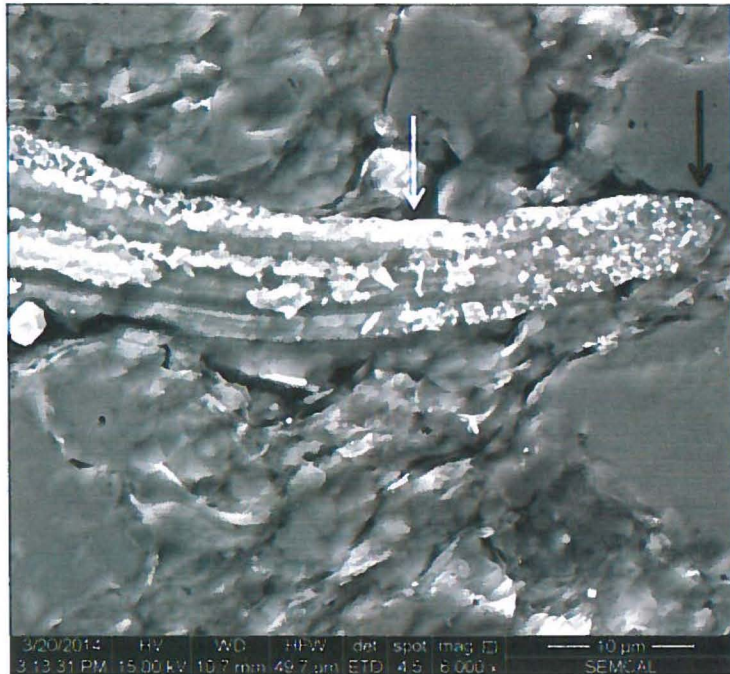
Figure 11-Clay rich zone showing typical linear pores (Arrows pointing at pores).



**Figure 12-Clay rich zone showing typical triangular pores (arrows pointing at pores).**

Carbonate-rich zones in gas shales can have abundant fossils which are also enriched in clay, contributing to porosity (Elgmati et al., 2011). As seen in the following images, fossils form micro-pores in different ways depending on what they are and what they are surrounded by.

Figure 13 shows an image where a fossil acts as a host environment for different pores around it.



**Figure 13- Pores associated with fossil (White arrow-pore with grain. Black arrow-mud matrix).**

In Figure 13, relatively large pores associated with an interface between a fossil and adjacent phases are shown. The nature of pores around the fossil is dependent upon the fossil type (e.g. shape, size, etc.). In areas where a fossil is surrounded by mud matrix, limited void space occurs. However, when it is adjacent to larger grains such as pyrite or silica grains, pore space is created in both pocket shapes and rectangular shapes of various length scales.





Figure 14 – Fossil displaying pores filled with organic matter inside of structures within fossil.

Figure 14 illustrates a different type of pore association involving fossil. The fossil itself contains micro and nano scale porosity internally. In addition, the shapes of the micro-pores are cubic-like and are 0.05–3 μm in size. Organic material was located within the fossil pores using EDS.

### III. Pyrite Formation

Pyrite forms in a variety of ways and can contribute to micro-pore structures (Curtis et al., 2012; Loucks et al., 2012; Kanitpanyacharoen et al., 2012). Framboidal pyrite is a biologically-derived morphological feature where pyrite crystals are bound together with pore sizes between 20 and 100 nm (Elgmati et al., 2011). Numerous examples of pyrite exhibiting this same texture, and common to many other gas shales, were observed.

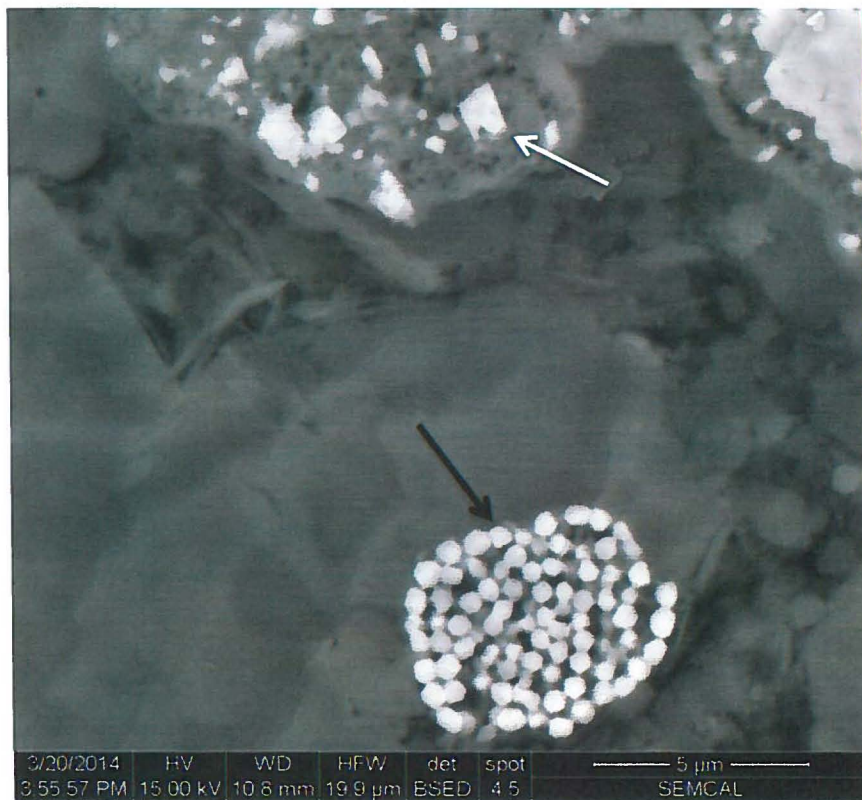


Figure 15- Disseminated pyrite (White arrow) and framboidal pyrite (black arrow).

In Figure 15, two different forms of pyrite are shown, each of which contributes to porosity in a different way. In the upper part of the image, disseminated pyrite can be seen while in the lower left part of the image, a pyrite framboid is observed. Upon close examination, the disseminated pyrite fills in the pore space. In contrast, the framboidal pyrite acts as a host for pores among pyrite grains while forming tight boundaries with other minerals.



## IV. Organic Material

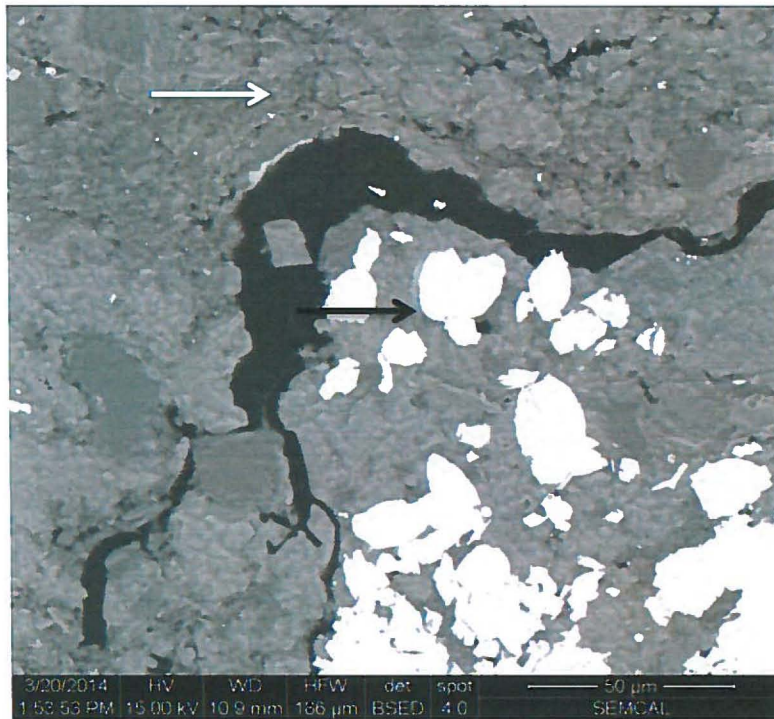
The presence and distribution of organic material is determined on the micro-scale with the aid of SEM images. Ion milled samples enhance the interpretation of sizes and shapes of organic material, along with the minerals that surround it. EDS data acquired from ion-milled samples coated with Au and Pd suggest that the material shown is indeed organic matter. The images below show different shapes and sizes of organic material occurring in a variety of mineral-hosted textures. Organic matter in gas shales typically occurs as a spongy texture containing pores that range from 10's of nm to micrometers (Loucks et al., 2012).



**Figure 16- Long, curvilinear string of organic matter (Arrow shows entrained pyrite).**

Figure 16 shows organic matter in a long and thin shape. Examples such as these are found throughout the 3000 ft depth sample. Size is quite variable in both length and width on the micro-to mesoscale (micrometers to 100's of micrometers). The organic matter's shape is generally curvilinear and exhibits smooth or semi-smooth boundaries. In this image, pyrite is entrained within the organic material. Furthermore, the organic material is associated with a

different mineralogical zone. This is unlike the spongy texture commonly described for other prominent gas shales (Loucks et al., 2012).



**Figure 17-Elongated pocket of organic matter (White arrow-clay rich. Black arrow-carbonate region).**

Figure 17 shows an elongated pocket of organic matter that is different in shape and size than the example in Figure 16. This type of organic-rich zone is wide in the center and pinches out at the edges. A clay-rich region is located above the organic matter in Figure 17. Below the organic matter there is a carbonate + pyrite-rich area. When one compares the occurrence of organic matter in the Utica Formation to other gas shales, the Utica appears to exhibit very different shapes and sizes. This variability in organic matter-mineral associations may produce differences in petrophysical properties.

## **4. Conclusions and Future Work**

### **I. Conclusions**

The first goal of this research was to develop a method to create a high quality surface polish of large areas in shale that are suitable for SEM imaging. Large areas are of interest because of the presence of extensive local textural and mineralogical differences even at the thin section scale. Because of the different hardness of phases contained in the shale, i.e., quartz, calcite, clay, and organic matter, this posed a significant challenge. It became clear that traditional grit-based polishing methods were not adequate. Considerable effort was devoted to developing a reproducible protocol for polishing shale samples using ion milling. The SEM images acquired from properly prepared ion milled samples permitted high resolution imaging of micro-features such as pores, clays, fossils, pyrite, and organic material.

Detailed SEM images of clay mineral assemblages, disseminated pyrite and pyrite framboids, carbonate-rich zones and organic matter were obtained from two representative samples of the Utica, one shallow and one deep in the Appalachian Basin in Ohio. The Utica formation appears to exhibit many of the same textural and mineralogical properties that have been observed in other gas shale formations in the United States. One exception to the similarities that the Utica Shale shares with other gas shales is the micro scale organic matter shape and size. These similarities imply that similar resource exploration and recovery practices used for other formations such as the Barnett and Eagle Ford can be applied to the Utica.



## II. Future work

Ion milling contributed to better surfaces in this methods development. In the future more work is needed to optimize the ion mill to minimize artifacts such as smearing and chiseling. Future work will also include acquisition of images from a variety of depths and locations. Images from large surface areas will allow for detailed image interpretation from more representative portions of 2.5 cm diameter samples, the typical size for side-wall core used by industry. Utilizing stitched images of large areas from different depths and locations will allow correlation of micro-features with depositional and burial diagenesis environments.

Results from the SEM images should also be combined with other analytical information. X-ray computed microtomography (XCT) provides good images of low density features such as porosity, fractures, and organic matter. While XCT can yield volume fraction of low-density features it becomes more difficult to quantify total volume of porosity, especially for pores at the sub-micron length scale (Kanitpanyacharoen et al., 2012). In the future combination of XCT with large scale imaging measurements will yield greater understanding of total volume of porosity and its relation to organic matter.

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